

FRACTIONATION OF ORGANIC SOLUTES IN OIL SHALE RETORT WATERS
FOR SORPTION STUDIES ON PROCESSED SHALE

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A frequently proposed method for disposing of aqueous effluents from oil shale processing is the use of these waters for moistening processed shale (1). This method of disposal is part of the recently approved development plan for leased oil shale tract C-a (2). Retort waters produced with the oil are a major component of shale processing waste water. Retort waters contain high concentrations of organic and inorganic solutes which present serious disposal and purification problems (3-7). Many studies have focussed on solutes which might leach from processed shale (8-10), but little attention has been paid to the fate and transport of retort water solutes incorporated into processed shale or present in in situ retorts. Of particular interest are the organic solutes because of their potential toxicity.

Studies of organic solute transport are complicated by the complex and variable natures of both the retort waters and the processed shales which result from many diverse retorting methods. The use of surface-retorted processed shale has been proposed for the disposal of waste waters from both surface and in situ retorting (2). Organic solutes found in retort waters have been determined by many different methods (3, 11-13). This study will present a unique organic solute characterization based on sorption of both a true in situ and a simulated in situ retort water. This characterization data is then applied to solute sorption studies on TOSCO-II processed shale.

TOSCO-II¹ processed shale was selected as the sorbent in this investigation because its small particle size and high surface area facilitated laboratory studies and because it was considered most likely to give the high sorptive capacities (as compared to other processed shales) needed for disposal of retort water. Retort waters were obtained from both the 150-ton simulated in situ retort and the Rock Springs site 9 in situ retort of the Laramie Energy Research Center.

An organic solute fractionation scheme (DOC fractionation analysis) based upon adsorption was developed specifically for this study (14). Natural organic solutes in surface and ground waters in the area of the Green River formation were characterized by DOC fractionation analysis to assess the impact of possible inputs of waste water from oil shale processing. The purpose of this report is to relate DOC fractionation analyses of retort waters to sorptive interactions with processed shale so that predictions can be made about the movement of organic solutes from processed shale to adjacent soils and waters.

EXPERIMENTAL

Retort Water and Shale Samples. TOSCO-II processed shale was obtained from the TOSCO Corp. Research Center in Golden, Colorado. Site 9 in situ retort water, designated OMEGA-9 (15), and 150-ton retort water (barrel 66, run 13) were obtained from the Laramie Energy Research Center. Previously filtered OMEGA-9 water was stored at 4°C in a plastic lined, sealed drum. 150-ton retort water samples were aliquoted from an oil-and water-containing drum stored at room temperature. Filtration of 150-ton water through glass fiber filters removed suspended oil. Production wells 3, 4, 8, and 9 at the Laramie Energy Research Center's Site 9 in situ retort were sampled in May 1977. The warm oil and water mixture pumped from the wells was chilled to 4°C and stored in glass bottles. Glass fiber filtration removed suspended oil before fractionation and analysis.

Water Analysis. The major inorganic solutes in the retort waters were determined by the U.S. Geological Survey Denver Central Laboratory (16). Most of these

¹ The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

data are available elsewhere, but the sulfur speciation of these waters has not been previously reported. Total sulfur was determined by a standard bromine in carbon tetrachloride digestion procedure (17). Sulfate was determined by a barium sulfate turbidimetric procedure (16). Thiosulfate was determined by iodimetric titrations. Raw waters as well as carbon filtered (to remove organic solutes) and zinc acetate treated (to precipitate any sulfide) water were titrated with standardized sodium triiodide. Sulfite was determined by the difference in equivalents of iodine consumed before and after addition of formaldehyde to complex any sulfite.

DOC Fractionations. DOC fractionation using macroreticular resins (5) was used to determine the distribution of organic solutes in the water samples. Analytical scale DOC fractionations were performed by Huffman Laboratories, Wheat Ridge, Colorado. Preparative scale fractionations of 150-ton and OMEGA-9 retort waters were conducted by a modification of the analytical scale method. In the modified procedure the acidification of the sample is accomplished on the H^+ form cation exchange column rather than by HCl addition. This eliminates CO_3 and HCO_3^- as CO_2 , whereas HCl addition introduces Cl^- ions which require later removal on a large anion exchange column. The procedure is outlined in figure 1. Samples of the retort waters were diluted to a concentration of 500 mg/L DOC with distilled water and fractionated. Ten liters of diluted OMEGA-9 water and 36 liters of 150-ton retort water were fractionated. Hydrophobic solutes were concentrated and fractionated on a 3,200 mL bed of Amberlite XAD-8, a nonionic macroreticular acrylic ester resin. Hydrophobic bases (HPO-B) were eluted with 0.1 N HCl, hydrophobic acids (HPO-A) with 0.5 N NH_4OH and hydrophobic neutrals (HPO-N) with methanol. Hydrophilic bases (HPI-B) were concentrated on a 2,300 mL column of H^+ form AG MP-50 (BioRad Laboratories) cation exchange resin and eluted in 0.5 N NH_4OH . Hydrophilic acids (HPI-A) were concentrated on a 1,000 mL bed of OH^- form AG MP-1 anion exchange resin and eluted with 0.5 N HCl. Hydrophilic neutrals (HPI-N) passed through all columns and were collected.

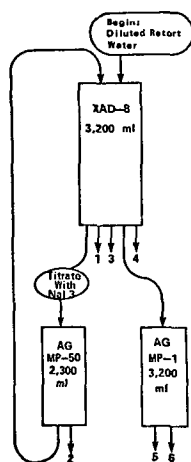


Figure 1.--Flow diagram of the fractionation of organic solutes in retort waters.
1. Hydrophobic bases, 2. Hydrophilic bases, 3. Hydrophobic acids,
4. Hydrophobic neutrals, 5. Hydrophilic neutrals, 6. Hydrophilic acids.

The procedure developed to fractionate retort waters on a large scale involves the addition of concentrated NaI_3 to the first XAD-8 eluate to destroy thiosulfate present. Thiosulfate dissociation to elemental sulfur and sulfite resulted in fouling of the cation exchange resin if this step was not included. The DOC concentrations of solutions derived from preparative fractionations were determined on a Beckman Model 915 carbon analyzer.

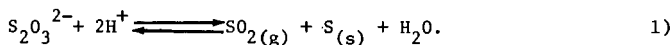
Sorption Studies. 150-ton retort water was diluted 1:10 ($\text{DOC}=500 \text{ mg/L}$) with distilled water. Weighed variable amounts of TOSCO-II processed shale were added to 200 mL volumes of the diluted retort water and the suspensions stirred for one week at 25°C in a water bath. After centrifugation aliquots of the supernatant solution were analyzed for DOC. Fractions of 150-ton retort water were diluted to a concentration (C_1) of organic solutes (as carbon) equal to 1/10 the concentration of that solute fraction in the original retort water. These solutions were brought to pH 8.65 and a specific conductance of $7,400 \text{ } \mu\text{mho/cm}$ at 20°C by the addition of $\text{NH}_4(\text{CO}_3)_2$ and HCl to provide an inorganic solute composition similar to that in ten-fold diluted 150-ton retort water. Aliquots (200 mL) of these diluted fractions were equilibrated by stirring for 1 week at 25°C with varying amounts of TOSCO-II processed shale. After centrifugation, the DOC concentration of the supernatant solutions were determined. The hydrophobic neutral fraction was not studied because these solutes are obtained from the fractionation in methanol and are insoluble in water.

Amounts of activated carbon (Calgon Filtrasorb 400) varying from 10 mg to 10 g were added to 200 mL volumes of 150-ton retort water diluted 1:10 with distilled water. The suspensions were stirred for 1 week at 25°C , centrifuged, and DOC determinations were run on the supernatant solutions.

RESULTS AND DISCUSSION

Retort Water Inorganic Solute Analysis. The major inorganic constituents of the retort waters are presented in table 1. It was necessary to determine these species to devise a workable fractionation procedure and to properly design adsorption experiments. OMEGA-9, the in situ retort water, differs from the 150-ton simulated in situ retort water mainly in having lower concentrations of ammonia, carbonate species and organic solutes, and in having a far larger concentration of sodium. 150-ton water displays the character of a distillate in containing no appreciable concentrations of nonvolatile cations. 150-ton water also has a higher total ionic solute concentration ($1,200 \text{ meq/L}$ vs 500 meq/L) than the OMEGA-9 water. The differences in Na concentration and in total solute content probably are a result of the dilution of OMEGA-9 by native saline ground water. Analytical data on the native ground waters at the site (3) support this hypothesis.

The presence of thiosulfate in these waters has not been previously reported and the authors feel there has been some confusion about the sulfur speciation in OMEGA-9. We were led to study the sulfur chemistry of the waters because the application of OMEGA-9 to H^+ form cation exchange columns in the DOC fractionation scheme resulted in the formation of a sulfur precipitate which fouled the resin. Acidification of the waters also causes this same sulfur yielding dissociation of thiosulfate:



Several qualitative and quantitative tests were used to verify the sulfur chemistry of OMEGA-9 water. The presence of thiosulfate was indicated by the formation of elemental sulfur upon acidification, by the characteristic behavior of thiosulfate solutions upon addition of silver ions, and by the ability of OMEGA-9 water to dissolve silver chloride after all ammonia has been removed. No sulfide was detectable in the water by lead acetate paper tests of steam from acidified retort water. Sulfide was undetectable by the addition of AgNO_3 solution to retort water (Ag_2S forms if sulfide is present). The total sulfur content ($2,300 \text{ mg/L}$) of OMEGA-9 matches the sum of the SO_4^{2-} (620 mg/L S as SO_4^{2-}) and $\text{S}_2\text{O}_3^{2-}$ ($1,700 \text{ mg/L}$ S as $\text{S}_2\text{O}_3^{2-}$) sulfur concentrations so that other S species must be at low levels

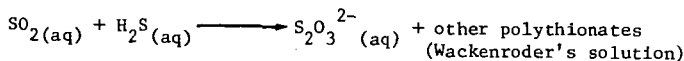
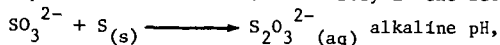
Table 1. Retort water solute analysis

Constituent	Barrel 66, run 13	OMEGA 9
	150-ton retort	In situ retort
pH	8.6	8.5
Specific Conductance (micromhos at 20°C)	48,000	25,800
Milligrams per liter		
Calcium (Ca)	4	8
Magnesium (Mg)	16	12
Sodium (Na)	188	4,100
Potassium (K)	24	43
Bicarbonate (HCO ₃)	33,400	15,100
Carbonate (CO ₃)	14,900	2,100
Chloride (Cl)	2,800	3,900
Fluoride (F)	12	56
Sulfate (SO ₄)	1,340	1,400
Thiosulfate (S ₂ O ₃)	2,050	3,000
Total Sulfur (S)	-----	2,300
Ammonium (NH ₄ as N)	-----	3,800
Total Kjeldahl Nitrogen (TKN)	18,000	4,000
Dissolved Organic Carbon (DOC)	5,000	1,000
Milliequivalents per liter		
NH ₄	1,280*	271
Ca	0.2	0.4
Mg	1.3	1.0
K	0.6	1.1
Na	8.2	178
Cation Sum	1,290.3	451.5
HCO ₃	547	247
CO ₃	498	70
Cl	79	110
F	0.6	2.9
SO ₄	27.9	29.1
S ₂ O ₃	36.6	53
Anion Sum	1,189.1	512.0

* NH₄ estimated from TKN

relative to S₂O₃²⁻ and SO₄²⁻. Results of iodimetric determinations of S₂O₃²⁻ were identical for raw samples, for carbon filtered (70 percent of DOC removed)³ and zinc acetate treated (to precipitate any sulfide which could also have oxidized NaI₃) samples. Sulfite was not present at detectable levels by iodimetry because consumption of iodine was identical before and after addition of formaldehyde which complexes any SO₂²⁻ present.

We can speculate on the origin of thiosulfate in retort water. Heated gasses containing SO₂ and steam probably contacted sulfides, H₂S or perhaps even elemental sulfur derived from the roasting of pyrite. These known aqueous solution reactions are perhaps clues to the sulfur chemistry in the retort:



Organic Solute Fractionation. DOC fractionation analysis was developed to serve as a compound classification based on sorption that fills the gap in organic solute characterization between organic solute concentration (DOC) and specific compound identification. Hydrophobic solutes are first isolated and fractionated into acid, base, and neutral components by physical adsorption and desorption on a macroreticular, acrylic ester resin. After removal of hydrophobic solutes from water, hydrophilic base and acid solutes are isolated by ion-exchange sorption on cation and anion exchange resins, respectively. Hydrophilic neutral solutes remain dissolved in the deionized water sample at the end of the fractionation sequence. Because DOC fractionation analysis is based on various sorptive interactions, it is a useful method for studying and defining the sorptive interactions which occur between retort water organic solutes and processed shale. In addition, the sorption studies have been simplified to six compound classes which are relatively homogeneous with respect to their sorptive interactions, as opposed to the impossible task of defining the sorptive interactions of each compound in retort water. Additional uses and interpretations of data from DOC fractionation analysis have been previously discussed (14), and table 2 lists the types of compounds likely to be found in each fraction.

Table 2. Compound classes in organic solute fractions

HPO-B:	Aromatic amines except pyridine,
HPO-A:	Aliphatic carboxylic acids > five carbons; aromatic carboxylic acids, phenols.
HPO-N:	Hydrocarbons, aliphatic alcohols, amides esters, ketones, and aldehydes of < five carbons, pyrroles, and indoles.
HPI-B:	Aliphatic amines, pyridine, amino acids.
HPI-A:	Aliphatic acids of < five carbons, polyfunctional acids.
HPI-N:	Aliphatic amides, alcohols, aldehydes esters, and ketones < five carbons. Polyfunctional alcohols, carbohydrates.

The analytical DOC fractionation data from 150-ton and OMEGA-9 retort water and a natural surface water are shown in table 3.

Table 3. Dissolved organic carbon fractionation analyses as percent of initial DOC

Fraction	150-ton retort Water (5,000 mg/L DOC)	OMEGA-9 Retort Water (1,000 mg/L DOC)	Piceance Creek at White River (9.1 mg/L DOC)
Hydrophobic solutes	65	49	51
Hydrophilic solutes	35	51	49
Hydrophobic bases	9	13	1
Hydrophobic acids	28	19	23
Hydrophobic neutrals	28	17	27
Hydrophilic bases	8	12	2
Hydrophilic acids	17	29	44
Hydrophilic neutrals	10	10	3

In the preparative scale fractionations the overall yield of organic solutes (based on DOC) obtained in the fractions was 85 percent for 150-ton retort water and 90 percent for OMEGA-9 water. The 150-ton retort water contains a higher concentration of hydrophobic solutes, with most of the difference appearing in

hydrophobic acids and neutrals. Hydrophobic acids can act as anionic detergents which would tend to increase the solubility of hydrophobic neutral species in water. The higher concentration of hydrophobic neutrals in 150-ton water is probably due to solubilization by hydrophobic acids.

The presence of significant concentrations of basic solutes distinguishes the solute distribution in these retort waters from that in most natural waters. Natural waters normally contain a hydrophilic base concentration of 1-10 percent of the total DOC, but hydrophobic bases are usually nearly undetectable (18). The data from the DOC fractionation of the Piceance Creek sample is typical of a natural surface water. Hydrophobic organic base concentrations in natural waters are generally low because such solutes are strongly adsorbed by cation exchange processes on most soils and sediments, and by hydrophobic interactions (19). Also, there are not as many natural sources for organic bases as there are for organic acids. The contamination of a natural water by retort water might be readily detectable by an increase in the level of hydrophobic base solutes.

Sorption Studies. The sorption isotherms presented in this study were generated by allowing solutions of identical initial organic solute concentration (C_i) to equilibrate with varying weights of sorbent, then measuring the equilibrium organic solute concentrations (C_{eq}). The sorptive capacity of the sorbent (mg organic carbon/g sorbent) is plotted as a function of C_{eq} . This experimental approach makes it possible to observe differences in the affinity of the sorbent for different components in a complex mixture of solutes. The data generated in this manner also provides better insight into the transport of a mixture of solutes through processed shale than the alternate experimental design in which the sorbent weight is held constant while C_i is varied. This experimental design is important because one of the goals of this study was to determine which types of organic solutes are strongly sorbed by the processed shale and which are not. All retort waters were diluted with distilled water to a $C_i = 500$ mg/L DOC to reduce organic solute-solute interactions so that the varied affinities of the different solute fractions might be better observed. Above $C_i = 500$ mg/L DOC, the DOC fractionation changed with increasing DOC, whereas below $C_i = 500$ mg/L DOC, the DOC fractionation remained essentially constant as DOC decreased.

TOSCO-II processed shale was compared with activated carbon to better evaluate its potential as a sorbent for the organic solutes in retort water. Sorption isotherms based on DOC for unfractionated 150-ton retort water on TOSCO-II processed shale and on Calgon Filtrasorb 400 activated carbon are shown in figure 2. The most significant result is that, on an equivalent weight basis, activated carbon has a far greater sorptive capacity for retort water organic solutes than processed shale, despite similarities in surface appearance. On an equivalent carbon basis using five percent non-carbonate carbon remaining in TOSCO-II processed shale, the shale has approximately half the sorptive capacities of activated carbon. An interesting feature of the processed shale sorption isotherms is the sudden increase in the slope of the curve at $C_{eq} = 400$ mg/L DOC ($C_{eq} = 80$ percent of C_i). This indicates that about 20 percent of the retort water DOC has a much higher affinity for TOSCO-II processed shale than the remaining 80 percent.

Sorption isotherms of the individual organic solute fractions derived from 150-ton retort water on TOSCO-II processed shale (figure 3) provide insight into specific sorptive processes. The most important aspect of the solute fraction isotherm data is the greater sorptive capacity of the shale for acid fractions than for base fractions, an unexpected result. Cation exchange properties of most natural soils and sediments normally results in higher sorptive capacities for bases than acids (7). The processed shale does not seem to exhibit this sorptive capacity for the bases in retort water. As expected, hydrophobic solute fractions are more strongly sorbed than hydrophilic fractions. The rapid increase in the slope of the unfractionated sorption isotherm (fig. 2) at $C_{eq} = 400$ mg/L DOC ($C_{eq} = 80$ percent of C_i) is probably due to the expected high affinity of the water insoluble hydrophobic neutral fraction for the processed shale. The individual fraction isotherms in figure 3 have been added to yield a fraction composite isotherm.

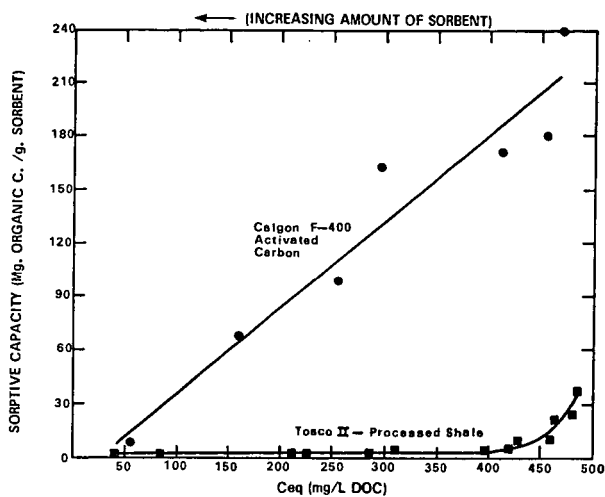


Figure 2.--Sorption of 150-ton retort water on Calgon F-400 and TOSCO II-processed shale.

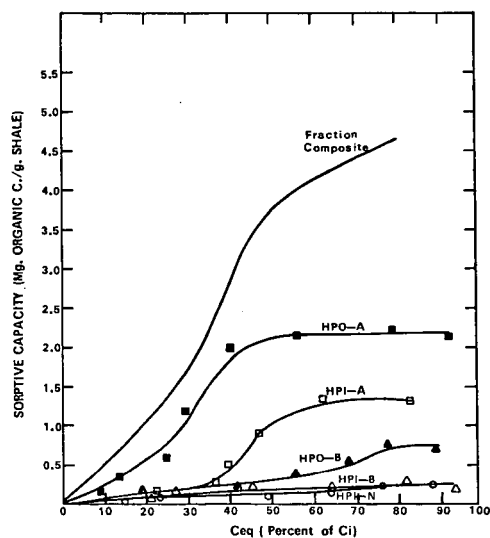


Figure 3.--Sorption of 150-ton retort water organic solute fractions on TOSCO II-processed shale.

Figure 4 compares the fraction composite isotherm with the unfractionated sorption isotherm. Below $C_{eq} = 80$ percent of C_i , the two isotherms represent sorptive capacities of the same magnitude but do not exactly coincide and the difference is very likely due to the absence of any contribution from the hydrophobic neutral fraction to the composite fraction isotherm. In the unfractionated sorption isotherm experiment the sorption of high affinity hydrophobic neutrals could result in a modified sorbent surface, different from that present in experiments on separate fractions. Differences between the composite and unfractionated data could also arise from solute-solute interactions. Above $C_{eq} = 80$ percent of C_i , the unfractionated sorption isotherm diverges greatly from the composite isotherm because of the high capacity of the shale for hydrophobic neutral solutes.

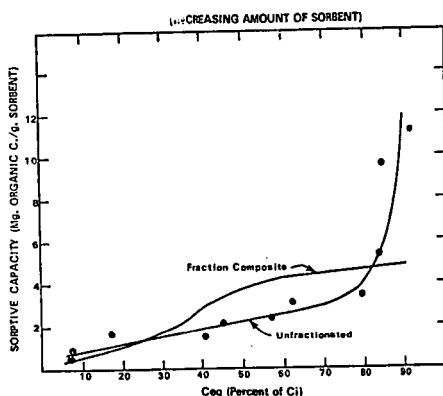


Figure 4.--Comparison of unfractionated versus fraction composite sorption isotherms of 150-ton retort water on TOSCO-II processed shale.

Rock Springs Site 9 Studies. Production wells 3, 4, 8, and 9 at the Rock Springs site 9 in situ retort were sampled for water in May 1977, approximately seven months after OMEGA-9 water was collected. The primary objective was to determine changes in organic solute composition with time. Table 4 presents the data from this study arranged in order of decreasing organic solute concentration (based on DOC) from left to right. The decrease in DOC and the shift in the hydrophobic-hydrophilic ratio seem to indicate that extensive dilution of the Site 9 retort water by native ground water has occurred in the seven months since collection of OMEGA-9. The most significant result here is that the hydrophobic base fraction has not been removed by sorption on the processed shale in the retort. This finding is in accord with the laboratory sorption data. Meaningful interpretations of other organic solute changes cannot be made because the system is complicated by inputs from the native ground water.

Thiosulfate was not detectable in water from any of the four wells. Sulfide and sulfite were also undetectable by iodimetry. A determination of sulfate and total sulfur content in water from one of the wells (no. 9) shows that essentially all sulfur present is in the form of sulfate. It is not known whether all thio-sulfate containing water has been effectively displaced by ground water, or whether an oxidative, microbial, or sorptive process is the cause of the disappearance.

Table 4. DOC Fractionation Analyses of Site 9 Ground Water as percent of initial DOC

Fraction	OMEGA-9 (1,000 mg/L DOC)	Well 3 (500 mg/L DOC)	Well 8 (140 mg/L DOC)	Well 4 (80 mg/L DOC)	Well 9 (120 mg/L DOC)	Ground-water composite collected before retorting
Hydrophobic solutes	49	62	63	66	65	71
Hydrophilic solutes	51	38	37	34	35	29
Hydrophobic bases	13	14	10	13	4	1
Hydrophobic acids	19	29	32	34	39	38
Hydrophobic neutrals	17	19	21	19	22	32
Hydrophilic bases	12	12	9	11	9	8
Hydrophilic acids	29	19	18	17	22	17
Hydrophilic neutrals	10	7	10	6	5	5

CONCLUSIONS

This study has presented a characterization of the organic solutes in retort water based on sorption processes and has identified some important features of the sorptive properties of TOSCO-II processed shale. Retort waters contain high concentrations of ammonia, organic bases, and thiosulfate, that are normally very low in natural waters. TOSCO-II processed shale sorbs organic acids preferentially to organic bases whereas the reverse is true in most soil systems.

TOSCO-II processed shale has a low overall sorptive capacity for retort water organic solutes when compared on an equal weight basis to activated carbon, despite similarities in appearance. The organic solute fractions most likely to pass through or run off TOSCO-II processed shale are the hydrophilic neutral, hydrophilic base and hydrophobic base fractions. Of most obvious environmental concern is the hydrophobic base fraction that is at low levels in natural waters. TOSCO-II processed shale is an effective sorbent for hydrophobic neutral species and thus will better retain hydrocarbonlike solutes. Polyaromatic hydrocarbons and neutral polynuclear heterocycles, refractory compounds of great environmental importance, would very likely be removed from oil shale waste waters by contact with TOSCO-II processed shale. This kind of information should be utilized in the design of waste-water disposal methods.

It appears that DOC fractionation analysis can provide useful information about the transport of retort water organic solutes from in situ retorts and about the migration of organic solutes from surface-disposed retort waters. The results of this work have led to other investigations into the surface chemistry of retorted oil shale and into the sorptive interactions of retort water solutes with soils and sediments. It is hoped that the research presented here will be the first step in developing a conceptual model of the transport organic solutes derived from retort water through processed shales, and later of their transport through soil systems.

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REFERENCES

- (1) Cameron Engineers, Inc., Synthetic Fuels Data Handbook; compiled by J. A. Hendrickson, p. 102, (1975).
- (2) Gulf Oil Corporation and Standard Oil (Indiana), Revised Detailed Development Plan for Tract C-A, Submitted to Area Oil Shale Supervisor, U.S. Geological Survey, (1977).
- (3) Harding, B. L., K. D. Linstedt, E. R. Bennett, and R. E. Poulson, Removal of ammonia and alkalinity from oil shale retort waters by the use of weak acid cation exchange resins. Proceedings of the Second Pacific Area Chemical Engineering Congress, Denver, Colorado, 1, p. 442-449, (1977).
- (4) Jackson, L. P., R. E. Poulson, T. J. Spedding, T. E. Phillips, and H. B. Jensen, H. B., Characteristics and possible roles of various waters significant to in situ oil shale processing, Quar. Colorado School of Mines, 70, no. 4, p. 105, (1975).
- (5) Murphy, C. L., A. L. Hines, and R. E. Poulson, Hot gas stripping of simulated in situ oil shale retort water: This symposium. (1975).
- (6) Neal, L. G., J. Cotter, R. D. Sung, and C. Prien, An evaluation of the pollution abatement technologies available for treatment of wastewater from oil shale processing, Proceedings of the 68th Annual Meeting of the American Institute of Chemical Engineers, Los Angeles, California, 32 pp., (1975).
- (7) Ossio, E., P. Fox, J. F. Thomas, and R. E. Poulson, Anaerobic fermentation of simulated in situ oil shale retort water, This symposium, (1975).
- (8) Amy, G., J. Thomas, and A. L. Hines, Leaching of organic residuals from simulated in situ retorted oil shale: This symposium, (1977).
- (9) Parker, H. W., R. M. Bethea, N. Guren, M. N. Gaydor, and J. C. Watts, Interactions between ground water in in situ retorted oil shale. Proceedings of the Second Pacific Area Chemical Engineering Congress, Denver, Colorado, 1, p. 450-454, (1977).
- (10) Ward, J. C., Water pollution potential of spent oil shale residues from above ground retorting: Colorado State University, (1972).
- (11) Ho, C. H., B. R. Clark, and M. R. Guerin, Direct analysis of organic compounds in aqueous by-products from fossil fuel conversion processes. Oil shale retorting, Synthane coal gasification, and COED coal liquefaction. J. Environ. Sci. and Health, 11, p. 481, (1976).
- (12) Pellizzari, E. D., N. P. Castillo, S. Willis, D. Smith, and J. T. Bursey, Identification of organic constituents in aqueous effluents from energy-related processes: This symposium, (1978).
- (13) Wen, C. S., Electrolytic processes of oil shale and its derivatives: Doctoral Dissertation, University of Southern California, 239 p., (1976).
- (14) Leenheer, J. A., and E. W. D. Huffman, Jr., Classification of organic solutes in water by using macroreticular resins. Jour. Res. U.S. Geol. Survey, 4, no. 6, p. 737-751, (1976).
- (15) Farrier, D. S., R. E. Poulson, Q. D. Skinner, and J. C. Adams, Acquisition, processing, and storage for environmental research of aqueous effluents derived from in situ oil shale processing, Proceedings of the Second Pacific Chemical Engineering Congress, Denver, Colorado, 2, p. 1031-5, (1977).
- (16) Techniques of Water Resources Investigations of the U.S. Geological Survey, Methods for the analysis of inorganic substances in water and fluvial sediments, In preparation, (1977).
- (17) Official Methods of Analysis of the Association of Official Analytical Chemists, 11th Ed., AOAC, p. 31, (1970).
- (18) Leenheer, J. A., Unpublished data. (1977).
- (19) Stevenson, F. J., Organic matter reactions involving pesticides in soil, Ch. 15 in ACS Symposium Series, no. 29, Bound and Conjugated Pesticide Residues, p. 180-207 (1975).